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Association of Stereoregular Poly(methyl methacrylates). 6. Double-Stranded Helical Structure of the Stereocomplex of Isotactic and Syndiotactic Poly(methyl methacrylate)

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In 1965 Liquori et al.[1] proposed a model of the stereocomplex of isotactic and syndiotactic poly(methyl methacrylate) (it- and st-PMMA). Although this model could not explain most experimental results, e.g., those of template polymerization,[2] no other models were published. However, Tadokoro et al.[3] expected the structure of the stereocomplex to be closely related to the double-stranded helix of it-PMMA, and recently, Spěváček and Schneider[4] reported that the results of their NMR study are compatible with this idea. In the present paper such a model of the stereocomplex, which is also mentioned by Vorenkamp et al.[5] of our laboratory, is further developed with the aid of energy calculations and X-ray diffraction.

Experimental Section

The synthesis of it-PMMA, st-PMMA, and the stereocomplex and the preparation of the crystalline oriented stereocomplex were described in ref 6. The fiber pattern and the structure of crystalline it-PMMA are given in ref. 7. A film specimen of st-PMMA, cast from a chloroform solution, was stretched to 300–400% in a water bath at 95 °C and, under tension or at constant length, was subsequently crystallized at room temperature for 0.5–2 h by absorption of chloroacetone or diethyl ketone vapor.[8]

Results and Discussion

The fiber pattern of the stereocomplex is presented in Figure 1. From the few broad reflections of the three observed layer lines, listed in Table I, interplanar distances of 9.2, 6.1, and 4.6 Å were determined. The distances are in agreement with a fiber period of 18.4 Å, which implies that the first layer line corresponding to this distance is too weak to be observed.

Association of it-PMMA and syndiotactic poly(methacrylic acid) (st-PMAA)[9,10] leads also to the formation of a stereocomplex. A fiber pattern of this stereocomplex is given in Figure 2. The fiber period calculated from the three layer lines is again 18.4 Å, and now the first layer line is clearly present. As the stereocomplex from it- and st-PMMA and that from it-PMMA and st-PMAA are considered to be basically the same,[10] this is another argument for the correctness of the assumed period of 18.4 Å for both stereocomplexes.

In Figure 3 the fiber pattern of st-PMMA crystallized in the presence of chloroacetone is shown. About 5 wt % chlorine was found in a crystalline sample of st-PMMA by elemental analysis. After heating such a sample to 90 °C, which is still 40 °C below T_g of pure st-PMMA, the crystallinity was lost, attended by a weight loss in accordance with elemental analysis. Moreover, st-PMMA crystallized in the presence of diethyl ketone showed a slightly different X-ray diffraction pattern. Therefore, we conclude that the solvent molecules are incorporated in the crystalline phase during solvent-induced crystallization of st-PMMA.

As the X-ray pattern of the stereocomplex resembles the pattern of st-PMMA more than of it-PMMA, it is assumed that the syndiotactic chain in the stereocomplex has a

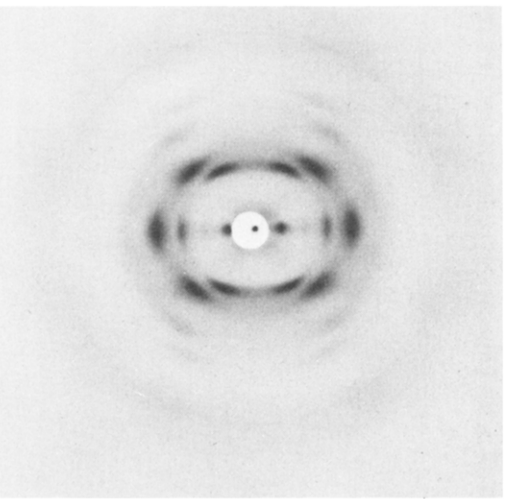

Figure 1. X-ray fiber pattern of the stereocomplex of it- and st-PMMA.

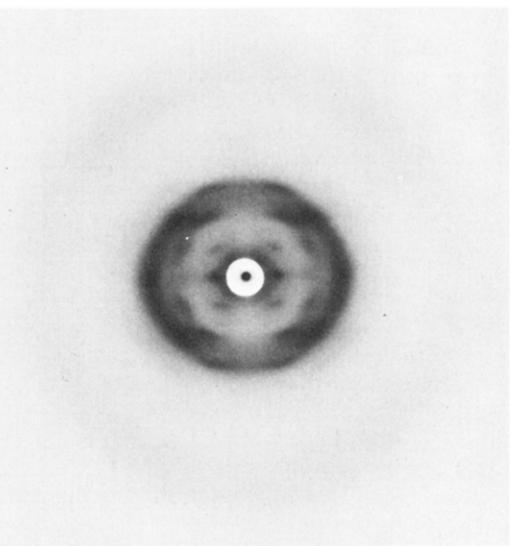

Figure 2. X-ray fiber pattern of the stereocomplex of it-PMMA and syndiotactic poly(methacrylic acid).

Table I
Observed Reflections in the X-ray Fiber Pattern of the Stereocomplex

layer line	*d*, Å	intensity
l = 0	20.9	strong
	10.9	very weak
	7.6	strong
	5.6	strong
l = 2	8.1	strong
	6.5	strong
l = 3	4.6	weak
l = 4	4.0	weak

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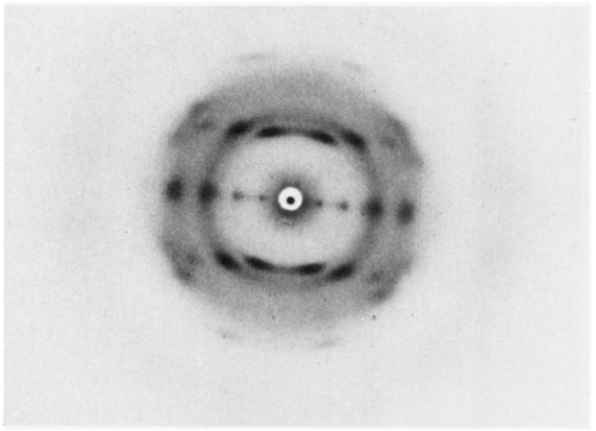

Figure 3. X-ray fiber pattern of solvent-induced crystalline st-PMMA.

conformation comparable to the conformation of st-PMMA after solvent-induced crystallization of st-PMMA and that the isotactic chain in the stereocomplex takes positions similar to those occupied by the solvent molecules in pure crystalline st-PMMA.

The interplanar distance in st-PMMA, calculated from the first layer line, is 9 Å and is comparable with the apparent 9.2-Å interplanar distance in the stereocomplex. However, it should be noted that the highest indexed reflections on the first layer line are split into two reflections, one above and one below this layer line, and therefore the real identity period of st-PMMA is much larger than 9 Å, as in the case of the stereocomplex.

Unfortunately, in the stereocomplexes no meridional reflections could be observed, so that the screw symmetry could not be obtained from these X-ray data and therefore the fiber pattern is compared with the fiber diagram of it-PMMA. In crystalline it-PMMA[7] 10 monomeric units correspond with a distance of 21.12 Å in the fiber direction. Therefore it seems reasonable to assume that about 8 monomeric units represent the fiber period of 18.4 Å in the stereocomplex.

The stereocomplex is assumed to be a double-stranded helix in which an isotactic chain with a small radius is surrounded by a syndiotactic chain with a large radius in such a way that the requirement of the ratio it/st = $^1/_2$ can be satisfied.[6]

Results from high-resolution solution and solid-state NMR[11] indicate that there are no specific interactions in the stereocomplex with respect to the pure components, so complex formation is only caused by a good steric fit of the two intertwined chains and the stabilization energy is due to nonbonding van der Waals and Coulombic interactions.

The conformational energy of the stereocomplex can now be calculated by the virtual bond method,[7,12] based on the assumption of a helix with an 8-fold symmetry and a pitch of 18.4 Å. The Cochran–Crick–Vand formula,[13] which describes the structure factor for helical polymers, predicts that in the case of distorted helices, intensities on layer lines can be very weak.[14] Therefore the lack of the first layer line on the X-ray pattern gives rise to the supposition that the helices in the stereocomplex are slightly distorted from the 8/1 helix. Therefore the screw symmetries of it-PMMA in the stereocomplex applied in the energy calculations were taken as 34/4, 32/4 (≡8/1), and 30/4. As the syndiotactic chain needs twice the number of residues compared with the isotactic one, the corresponding screw symmetries of st-PMMA in the stereocomplex should by 68/4, 64/4, and 60/4, respectively.

Table II
Geometrical Parameters of it-PMMA and st-PMMA in Their Stereocomplex

	it-PMMA	st-PMMA
bond angle θ_i'', deg	124	123
bond angle θ_{i+2}'', deg	120	121
backbone rotation angle φ_{i-1}, deg	15	−5
backbone rotation angle φ_i, deg	40	−50
backbone rotation angle φ_{i+1}, deg	20	−20
backbone rotation angle φ_{i+2}, deg	30	100
side-group rotation angle χ_{i-1}, deg	−5	10
side-group rotation angle χ_{i+1}, deg	−15	195
stereocomplex rotation angle, deg	210	
stereocomplex translation, Å	1.2	

Now the virtual bond method was applied to an it-PMMA and the corresponding st-PMMA chain separately. A great number of it- and st-PMMA chains of low conformational energy were brought together mathematically and the stabilization energy was calculated. As the two intertwined chains are not identical, contrary to the pure it-PMMA double helix, the position of the chains are varied with respect to each other by a rotation about the joined helix axis and a translation in the direction of the helix axis. From a tremendous number of calculations, the stereocomplex composed of an isotactic 30/4 helix and a syndiotactic 60/4 helix appeared to have the lowest conformational energy with a stabilization energy of 10.2 kJ/(base mol), which is attributed mainly to nonbonded interactions of CH_2 groups and ester groups. The data of the geometrical parameters for it-PMMA, st-PMMA, and their stereocomplex are listed in Table II.

The distance between two equal carbon atoms of the backbone (C*–C* or αC–αC) is about 2.5 Å. This means that a planar zigzag chain has an identity period of 2.5 Å and 7.35 units fill the distance of 18.4 Å. As a 30/4 helix has 7.5 units per 18.4 Å, the isotactic chain has a nearly extended conformation. Only the small backbone rotational angles in combination with the enlarged bond angles (Table II) give rise to the helical conformation. If the number of units per turn is increased, as in the case of 32/4–64/4 or 34/4–68/4 helices, the conformational energies of the components increase and the stabilization energies of the complex decrease more than 1 kJ/(base mol).

Just as in the case of it-PMMA[7] it is possible to screw the two helices through each other, and the energy barrier for screwing the it-PMMA and st-PMMA through each other, calculated in the same way as described for it-PMMA,[7] is only 0.8 kJ/(base mol). This low energy barrier may give an indication of a screw mechanism for stereocomplex formation in solution and in bulk. To prove the double-stranded model, a Fourier synthesis should be performed. However, as the number of observed reflections is too small to establish the unit cell, such a synthesis is not possible.

Conclusion

The stereocomplex of it- and st-PMMA probably consists of a double-stranded helix in which the isotactic chain with a 30/4 helical conformation is surrounded by a syndiotactic chain with a 60/4 helical conformation, the real fiber period being 4 × 18.4 = 73.6 Å. In Figure 4 a stereoview of the stereocomplex is shown. As in this model the isotactic chain is the inner chain, a modification of the ester groups of this chain will have a much greater influence than the change of the ester groups of the outer chain, which is in accordance with the results of Bosscher et al.[10]

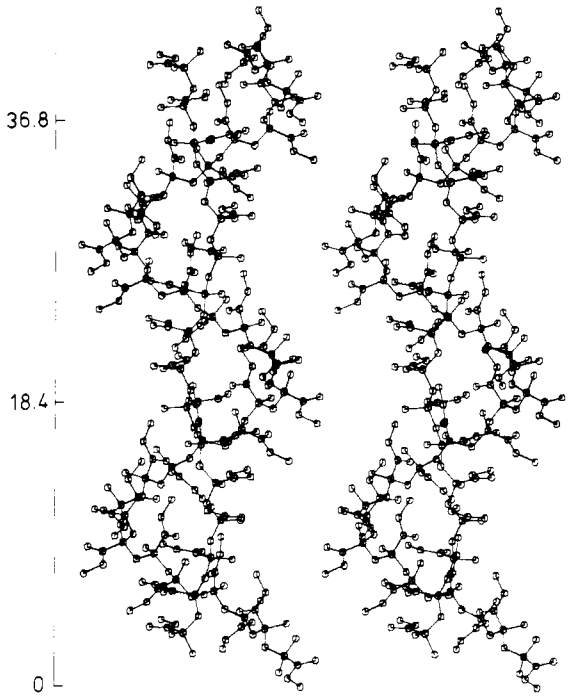

Figure 4. Stereoview of the stereocomplex of it- and st-PMMA (distances are given in Å).

Therefore, the stereocomplex formation can take place with it-PMMA and several syndiotactic methacrylic chains. The packing of different stereocomplex chains in a unit cell must be regarded as a hexagonal packing of rods, comparable with that of it-PMMA. However, the chains are not only shifted but also rotated with respect to each other to obtain a good steric fit. Therefore in the equatorial reflections no systematic extinctions, as in the case of it-PMMA, occur.

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Temperature Coefficients of Unperturbed Chain Dimensions. Helical Wormlike Chains

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In a series of papers on the helical wormlike (HW) chain,[1,2] we have shown that it can mimic the equilibrium conformational behavior of real chains as well as the rotational isomeric state (RIS) model.[3] In the study of chain conformations, the temperature coefficients of unperturbed chain dimensions along with the characteristic ratios provide valuable information, and both are the primary subjects of theoretical evaluation on the basis of the RIS model. In this note, therefore, we make a further test of the validity of the HW model with respect to the temperature coefficient of the mean-square end-to-end distance. Besides this, it is necessary to establish the temperature dependences of the model parameters in order to evaluate, for instance, the activation energies for local chain motions on the basis of the (discrete) HW chain.[4]

We consider the HW chain of contour length L. The basic model parameters are the constant curvature κ_0 and torsion τ_0 of its characteristic helix,[1] the stiffness parameter λ^{-1}, and Poisson's ratio σ of the chain as an elastic wire. λ^{-1} is defined by

$$\lambda^{-1} = 2\alpha/kT \tag{1}$$

where α ($=\pi d^4E/64$) is the bending force constant (with d the diameter of the cylindrical wire and E Young's modulus), k is the Boltzmann constant, and T is the absolute temperature. We assume that $\sigma = 0$, as in most of the cases studied previously and, for convenience, measure L, κ_0^{-1}, and τ_0^{-1} in units of the length λ^{-1}

$$\begin{aligned} L &= \lambda L' \\ \kappa_0 &= \lambda^{-1}\kappa_0' \\ \tau_0 &= \lambda^{-1}\tau_0' \end{aligned} \tag{2}$$

the primed quantities being unreduced. Then the coil limiting value $\langle R^2\rangle_C$ of the (unreduced, unperturbed) mean-square end-to-end distance $\langle R^2\rangle$ is given by[1,2]

$$\begin{aligned} \langle R^2\rangle_C/L &\equiv \lim_{L\to\infty} (\langle R^2\rangle/L) \\ &= (4 + \tau_0^2)/(4 + \kappa_0^2 + \tau_0^2)\lambda^2 \end{aligned} \tag{3}$$

Now, as far as the hypothetical elastic wire model is adopted, the temperature coefficients of L', $\kappa_0'^{-1}$, and $\tau_0'^{-1}$ must be of the same order of magnitude as linear thermal expansion coefficients of ordinary solids (10^{-6}–10^{-5} deg^{-1}), so that their temperature dependences may be ignored completely. Then, if we assume that α is also independent of temperature, we have

$$\frac{\mathrm{d}\ln\langle R^2\rangle_C}{\mathrm{d}T} = -\frac{16 - 4\kappa_0^2 + (8 + \kappa_0^2 + \tau_0^2)\tau_0^2}{(4 + \tau_0^2)(4 + \kappa_0^2 + \tau_0^2)}T^{-1} \tag{4}$$

In the sixth column of Table I are given values of the temperature coefficient calculated from eq 4 at given temperatures (in the fifth column) with the values of the model parameters (in the second and third columns) determined previously[1,2,5–7] for polymethylene (PM), poly(dimethylsiloxane) (PDMS), poly(oxymethylene) (POM), isotactic and syndiotactic polypropylene (i- and s-PP), isotactic and syndiotactic polystyrene (i- and s-PS), isotactic, atactic, and syndiotactic poly(methyl methacrylate) (i-, a-, and s-PMMA), and poly(DL-alanine) (PDLA). The observed values[8–11,13–19] are given in the last column, where the values for POM are the RIS ones.[12] The agreement between the calculated and observed values is rather good for some of them, but not always for others. However, the assumption that α is independent of T seems valid as a first approximation for these ordinary flexible polymers. We note that for the Kratky–Porod (KP) wormlike chain,[20] which is a special case of the HW chain with $\kappa_0 = 0$, the

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